

Uranium dynamics in biostimulated field-site sediments: Spatial distribution and formation of non-uraninite U(IV) phases

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The fate of U released in the environment is determined by a complex array of complexation, adsorption, redox, and precipitation reactions. Reduction of soluble U^{VI} species to U^{IV} by direct or indirect bacterial activity often results in the precipitation of U^{IV}O₂ (uraninite) and has been explored as an immobilization strategy for subsurface U plumes. We will present results from a three year experiment in which the biogeochemical conditions in U-contaminated groundwater and sediments from a field site at Oak Ridge National Laboratory (U.S.A.) were allowed to evolve in diffusion limited reactors under iron- and sulfate-reducing conditions. The reactors were amended with ethanol at the water-sediment interface, mimicking the injection of electron donor during *in situ* subsurface remediation by biostimulation. Synchrotron x-ray absorption spectroscopy (XANES and EXAFS) was used to track *in situ* the spatial distribution, valence state, and speciation of U and Fe in the reduction zone propagating into the sediment, in parallel with measurements of solution phase [SO₄], [U], [ethanol], and pH. Results show rapid initial reduction of Fe^{III} and U^{VI} in the sediment near the interface, as well as redistribution of U^{VI} in the areas ahead of the reduction front. Sulfate removal from the solution phase and U^{VI} reduction throughout the sediment continued for two years. EXAFS spectroscopy demonstrated that U^{IV} in the reduced sediment was present as a non-uraninite U^{IV} species, similar to the non-uraninite U^{IV} species detected in sediment samples collected from the injection wells during field-scale biostimulation campaigns at Oak Ridge National Laboratory. The immobilization of U^{IV} as a non-uraninite species in natural settings has important implications for the post-remediation stability of U plumes.

Sulfur speciation in lunar apatite

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Apatite incorporates several volatile elements (including S, as SO₄²⁻) and can provide a record of magmatic volatile evolution. Recent measurements of volatiles in apatite from Apollo sample 14053.241 revealed 300-450 ppm S. Although many lunar melts have sufficient S for sulfide saturation, the observed S content of lunar apatite is surprising because lunar samples (especially 14053) are highly reduced (\leq IW) and are thus expected to contain little SO₄²⁻. One possibility is that there are micro-environments in late-stage lunar melts that are more oxidized than one would infer from conditions recorded by other components of these rocks. Alternatively, it may be that S²⁻ substitutes for F+Cl+OH in lunar apatite: S²⁻-bearing apatite has been synthesized, but to our knowledge has not been observed in nature.

The K α X-ray wavelength can be used to determine the relative amounts of S²⁻ and SO₄²⁻ in lunar apatite. Analyses were conducted at Caltech (JEOL 8200 with a 15 kV, 300nA, 15 μ m defocused beam, at 30 s/step, using PET crystals), referenced to FeS₂, CaSO₄, and SO₄²⁻-rich Durango apatite.

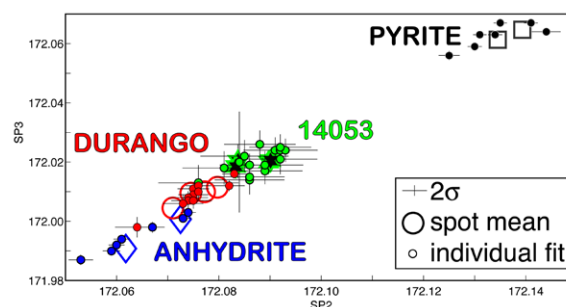


Figure 1: S K α peak position (L-value) for two spectrometers.

The K α peak of S in 14053 apatite is consistently shifted toward sulfide relative to both anhydrite (Δ = 29-44%) and Durango apatite (Δ = 19-24%; presumably containing all sulfur as sulfate) standards. This may indicate the first observation of a sulfide component in natural apatite. However, large uncertainties and apparent matrix effects (offset between anhydrite and Durango apatite) demand more data. Nevertheless, taking these data at face value indicates that lunar apatite includes both a S²⁻ and SO₄²⁻ component, in sub-equal proportions. The apparent SO₄²⁻ component in lunar apatite may indicate the presence of SO₄²⁻ in the late-stage lunar melt from which this apatite crystallized.